

curic isobutyrate, mercuric propionate, mercuric octoate, mercuric oleate, mercuric stearate, mercuric oxalate, mercuric adipate, mercuric benzoate, mercuric anthranilate, phenyl mercuric chloride, phenyl mercuric nitrate, mercuric naphthenate and phenyl mercuric oleate. This catalyst may be used in amount of from about 0.01 percent to about 0.4 percent, preferably about 0.10 percent by weight based on the weight of the resin.

With this catalyst there may be used a catalyst effective to cause rapid but limited initial build up in viscosity or precursor gellation. Such catalysts may include triethylene diamine, N,N,N'N' tetramethylene butane diamine, dibutyl tin dilaurate, stannous octoate and lead naphthenate. These materials will ordinarily be used in proportion of from about 0.002 percent to about 0.7 percent by weight based on the weight of the resin.

The use of a rapid catalyst such as a tin compound is believed to reduce the disparity between the rate of reaction of the isocyanate and the polyester or polyether polyol on the one hand and the rate of reaction between the isocyanate and the short chain diol modifier on the other hand and to give best product quality. Rapid catalysts are also effective to speed up the reaction between the isocyanate with hydroxyl terminated compounds so that the tendencies for the isocyanate to be extruded into the inert liquid of the discontinuous phase is reduced. The rapid reaction also enables the cover sheet 26 to be removed in a very brief space and the combination of rapid catalyst and catalyst having an induction period operates so that the composite of fibrous backing sheet 38 and solidified emulsion layer 18 will reach a condition in which it can be handled in a minimum time. It is to be observed that the tin catalyst tends to give immediate action and that there is evidence that the mercury catalyst slows the action of the tin catalyst so that time is available for forming the emulsion layer.

The following examples are given to aid in understanding the invention but it is to be understood that the invention is not restricted to the materials, proportions or procedures of the examples.

EXAMPLE 1

130 grams (0.0844 mols) of -NCO terminated prepolymer prepared by reaction of p,p'-diphenyl methane diisocyanate and hydroxyl terminated polybutylene adipate in a mol ratio of 2:1, resulting prepolymer having molecular weight of 1,540, and being solid at room temperature was liquefied and degassed at 100°C. and mixed with 3.9 grams of an emulsifier defined as blended polypropoxy/polyethoxy ether having an hydroxyl number of 20 which is a solid at 25°C. and the mixture was brought to a temperature of 100°C. 148 cc. of a liquid, paraffinic hydrocarbon mixture (boiling range 346°F. to 405°F.) was added slowly to the heated mixture of polybutylene adipate and the emulsifier with vigorous agitation to form an emulsion with the hydrocarbon as the internal phase. 7.75 grams (0.0860 mols) of 1,4 butane diol, about 7 grams of methyl isobutyl ketone and about 0.26 grams of an organosilicone block copolymer surfactant were added and mixed in. The resulting reactive emulsion was at a temperature of 100° C. and was supplied through a nozzle to the space between a casting sheet of release paper and an upper cover sheet of release paper, the surface of the cover

sheet having been wet with the liquid paraffinic hydrocarbon mixture forming the internal phase of the emulsion, the layer of emulsion being 0.08 inch in thickness. The layer was carried by the cover sheet between cooled aluminum plate maintained at a temperature of 75°C. After 7 minutes, the cover sheet was stripped from the layer of emulsion and the temperature of the emulsion layer was increased 100°C. After 30 minutes at this temperature a napped and sheared cotton sateen backer which had been wet with naphtha and squeezed to remove excess naphtha was laid on the surface of the emulsion. The assembly was held in a closed condition which inhibited naphtha evaporation and was stripped from the casting sheet and held in an oven at 100°C. for 24 hours to complete curing of the layer and evaporation of the hydrocarbon layer of the composite sheet. An excellent backed microporous polyurethane sheet material was obtained.

EXAMPLE 2

An emulsion of the prepolymer, emulsifier and liquid paraffinic hydrocarbon mixture, butane diol and surfactant was prepared as in Example 1 with the addition of a commercial tin catalyst for the reaction of isocyanate and hydroxyl in amount of 20 parts of catalyst per million parts of polyurethane and the emulsion was supplied at a temperature of 60°C. between a casting sheet and a cover sheet as a layer about 0.02 inch in thickness. The emulsion layer, with the casting and cover sheets in place, was passed in contact with cooled aluminum plates maintain at a temperature of 45°C. The cover sheet was stripped off after 15 seconds and the layer of emulsion was brought to 50°C. for 1 minute. At this point, a nonwoven polyester fiber sheet was laid on the exposed phase of the emulsion layer and the assembly was brought to 100°C. After 8 minutes at 100°C., the backer and solidified emulsion layer were stripped from the casting sheet and air dried at 100°C. for 30 minutes. The resulting sheet was a fine microporous polyurethane backed sheet material.

EXAMPLE 3

The procedure of Example 2 was repeated; but there was also included 1,500 parts per million of a mercury salt of a carboxylic acid as well as the tin catalyst. The emulsion was supplied between the casting sheet and the cover sheet at a temperature of 55°C. and the composite of casting sheet emulsion layer and cover sheet were passed between cooled aluminum plates maintained at 35°C. After 25 seconds the cover sheet was peeled off and the emulsion layer was brought to a temperature of 60°C. After 4 minutes at this temperature a stitch bonded continuous filament polyester nonwoven fabric was laid on the emulsion layer. This assembly was held at 115°C. for 5 minutes in a closed chamber which inhibited evaporation and was then stripped from the carrier sheet and pressed in an oven at 100°C. for 25 minutes to evaporate the liquid hydrocarbon and complete the cure of the polyurethane of the emulsion layer.

Having thus described my invention what I claim as new and desire to secure as Letters Patent of the United States is:

1. The process of forming a microporous sheet of solid polyurethane comprising the steps of casting an emulsion of fine droplets of a volatile organic liquid as the internal phase in a continuous phase comprising re-